



Oxygen storage capacity of CuMO₂ (M = Al, Fe, Mn, Ga) with a delafossite-type structure

Sumio Kato ^{a,*}, Ryu Fujimaki ^a, Masataka Ogasawara ^a, Takashi Wakabayashi ^b,
Yuunosuke Nakahara ^b, Shinichi Nakata ^a

^a Department of Engineering in Applied Chemistry, Faculty of Engineering and Resource Science, Akita University, 1-1 Tegatagakuen-cho, Akita 010-8502, Japan

^b Catalysts Division, Mitsui Mining & Smelting Co., Ltd., 1013-1 Ageoshimo, Ageo, Saitama 362-0025, Japan

ARTICLE INFO

Article history:

Received 15 July 2008

Received in revised form 4 November 2008

Accepted 28 November 2008

Available online 6 December 2008

Keywords:

Oxygen storage capacity

Delafossite

Oxidation/reduction cycle

ABSTRACT

Delafossite-type CuMO₂ (M: trivalent cation) compounds were synthesized and found to exhibit oxygen storage capacity under oxidation/reduction cycle. The oxygen storage capacity values of CuFeO₂ and CuMnO₂ at lower temperature were larger than those of CuAlO₂, CuGaO₂- and CeO₂-based materials. The large OSC includes an oxygen uptake at low temperature attributed to formation of metallic Cu by decomposition of the delafossite phase for CuFeO₂ and CuMnO₂. In the case of CuAlO₂, which remained without decomposition below 800 °C, the oxygen uptake increased with temperature up to 0.13 mol-O/mol-CuMO₂. The stability of the delafossite-type CuMO₂ against oxidation/reduction cycle is affected by M³⁺. In this study, it was found that the oxygen storage behavior of CuMO₂ can be controlled by a combination of Cu and M ions.

© 2008 Elsevier B.V. All rights reserved.

1. Introduction

Pollutants in automobile exhaust gas, including carbon monoxide (CO), nitrogen oxides (NO_x) and hydrocarbons (HC), are removed by a three-way catalyst (TWC) composed of precious metal catalyst and promoters supported on Al₂O₃. TWC performance is affected by compositional fluctuation of the exhaust gas. In the pollutant removal process, CO and HC are oxidized to CO₂ and H₂O, and NO_x is reduced to N₂. Therefore, the conversions of CO and HC decrease in reductive atmosphere, while conversion of NO_x decreases in oxidative atmosphere.

In order to enhance TWC performance by suppression of the cyclic oxidative (lean)-reductive (rich) compositional fluctuation in exhaust gas, metal oxides whose oxidation state can change easily have been used. At present, CeO₂-based solid solutions are widely used as promoters having oxygen storage capacity (OSC) [1,2]. CeO₂ exhibits oxygen storage/release behavior in oxidative/reductive atmosphere, which is accompanied by the redox of Ce ions between the oxidation states of Ce³⁺ and Ce⁴⁺. CeO₂-Al₂O₃ composite and perovskite-type oxides were also reported as new-type OSC materials [3,4]. Although it was found that copper/copper oxide system had oxygen storage/release ability in an automobile exhaust system, it caused fragmentation due to large volume change [5]. As non-stoichiometric fluorite-type CeO_{2-x} phase can

stably form in reductive atmosphere, the volume change of CeO_{2-x} accompanying the redox of Ce³⁺/Ce⁴⁺ is smaller than that in the case of a metal/metal oxide such as Cu/CuO. Therefore, CeO₂ is stable enough during oxygen storage/release process for use in an actual exhaust gas. Improvement of catalytic performance, especially of catalytic activity at low temperature and under oxygen-rich condition, has become necessary for compliance with recent automobile emission regulations. In order to improve activity at low temperature, it would be effective to use a promoter which exhibits a large OSC in the low temperature range. Therefore, Cu-containing oxides are suitable as promoters because they enable the reduction of Cu²⁺ to Cu⁺ to occur in a lower temperature range than that of Ce⁴⁺ to Ce³⁺. As pointed out above, oxidation and reduction reactions between copper and a copper oxide involve a large volume change that leads to fragmentation of the catalyst. Therefore, a metal oxide without large structural transformation during oxidation/reduction cycle would be suitable as the TWC promoter.

In order to develop a material exhibiting oxygen storage/release behavior at lower temperature, we focused on Cu-containing delafossite-type oxides expressed by the general formula CuMO₂ (M = trivalent cation) for use as OSC materials. Fig. 1 shows the crystal structure of 3R-type delafossite, CuFeO₂. CuMO₂ has a layered structure consisting of edge-shared MO₆ octahedra and two-coordinated Cu⁺ cations at the interlayer sites. There have been reported non-stoichiometric delafossite-type oxides such as CuLaO_{2+x}, CuYO_{2+x} and CuFeO_{2+x} which have extra oxide ions at the interlayer between MO₆ octahedra sheets [6,7]. This intercalation

* Corresponding author.

E-mail address: s_kato@ipc.akita-u.ac.jp (S. Kato).

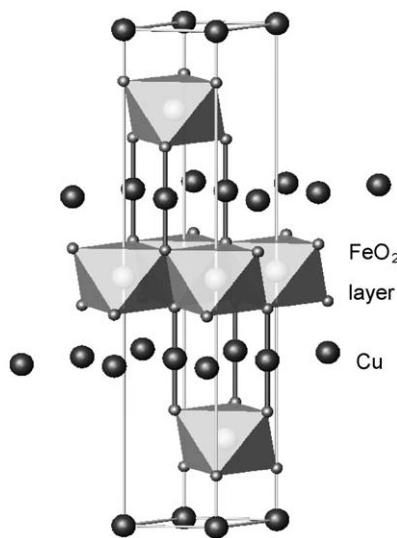


Fig. 1. Crystal structure of 3R-type CuFeO₂.

of oxide ions accompanies oxidation of Cu⁺ to Cu²⁺. Although change in oxygen storage and release behavior with temperature in air has been reported for CuLnO₂ (Ln: La, Y, Pr, Nd, Sm, Eu, Sc) [8–10], the behavior in cyclic oxidative–reductive atmosphere has not been investigated.

In this work, we synthesized delafossite-type copper oxides, CuMO₂ (M = Al, Mn, Fe, Ga), and investigated their OSC under cyclic oxidative–reductive atmosphere using a pulse injection method. Phase stability of the delafossite oxides against both oxidative and reductive atmospheres was also investigated in order to find a candidate material for a TWC promoter.

2. Experimental

CuMO₂ (M = Al, Fe, Ga, Mn) compounds were synthesized by a conventional solid state reaction. Cu₂O, Al₂O₃, Fe₂O₃, Ga₂O₃, and MnCO₃ were used as starting materials. The stoichiometric mixtures were obtained by ball milling using ethanol and pressed into pellets of 10 mm diameter. The pellets were heated at 860–1150 °C for 6–36 h in N₂ flowing at 200 cm³/min. In order to enhance the synthetic reaction, grinding, reforming and firing processes were repeated several times. Phase identification of the oxides was performed by a powder X-ray diffraction (XRD) method using Ni-filtered Cu K α radiation (RIGAKU RAD-C and MiniFlex diffractometer). Weight change of samples was measured by thermogravimetry (TG-DTA, RIGAKU TG8120, heating rate 10 °C/min) and specific surface areas of samples were estimated by N₂ adsorption method (Nippon BEL, Belsorp Mini II).

The OSC of each oxide was estimated by the pulse injection method according to Yao and Yu Yao [1], using H₂ gas instead of CO. This OSC value was used as an index of reversible oxygen uptake in the oxidation/reduction cycle. The oxide sample (25–50 mg) was placed in a quartz reactor and heated in He flow (200 cm³/min) at 800 °C for 15 min prior to pulse injection. Then, it was completely oxidized by injecting 50% O₂/He pulses until a 100% breakthrough was attained. H₂ and 50% O₂/He pulses were alternately injected into the oxide with He gas flowing at 200 cm³/min until constant O₂ uptake was found. The volume of a pulse was 1.16 cm³. The amounts of O₂ and H₂ in the effluent gas were monitored with a gas chromatograph (Shimadzu GC8A) equipped with a TCD detector. OSC of the oxide was estimated from the amount of O₂ uptake at 200–800 °C. The dynamic reduction behavior was evaluated by temperature-programmed reduction (TPR), which was performed

using a fixed bed flow system. The oxide sample (~50 mg) was placed in a quartz reactor and heated at 10 °C/min in a stream of 3% H₂/He (100 cm³/min) in the temperature range 100–800 °C. The amount of H₂ in the effluent gas through the oxide was monitored with a TCD detector. A liquid N₂-trap was attached in a gas line between the reactor and the detector to remove H₂O in the effluent gas.

3. Results and discussion

3.1. Synthesis and OSC of CuMO₂ (M = Al, Fe, Ga, Mn)

Fig. 2 shows XRD patterns for CuMO₂ (M = Al, Fe, Ga, Mn) compounds, which were synthesized under the conditions set out in Table 1. The formation of 3R-delafossite-type oxides was confirmed from the XRD patterns for CuAlO₂, CuFeO₂ and CuGaO₂ by comparison with ICDD-PDF files 39-0246, 35-1401 and 41-0255 for CuFeO₂, CuAlO₂ and CuGaO₂, respectively. For CuMnO₂, the diffraction peaks were indexed on the basis of a monoclinic unit cell. This result corresponds to a delafossite-type structure with a distortion of MnO₆ octahedra due to the Jahn-Teller effect of Mn³⁺ [11].

The oxygen storage capacities of CuMO₂ estimated as a function of temperature by the pulse injection are shown in Fig. 3. Specific surface areas of CuMO₂ were listed in Table 1. Oxygen storage behavior was observed at 300 °C for CuFeO₂ and CuMnO₂. OSC of CuFeO₂ and CuMnO₂ was 120 and 265 μmol-O₂/g at 300 °C, respectively, and increased with temperature to 500 °C. In the temperature range from 500 to 700 °C, CuFeO₂ and CuMnO₂ showed higher OSC of over 700 μmol-O₂/g. However, decrease of OSC was observed for CuFeO₂ above 700 °C. The OSC of CuGaO₂ and CuAlO₂ was less than 100 μmol-O₂/g below 500 °C and increased steeply at 600 °C for CuGaO₂ and at 800 °C for CuAlO₂. In the case of

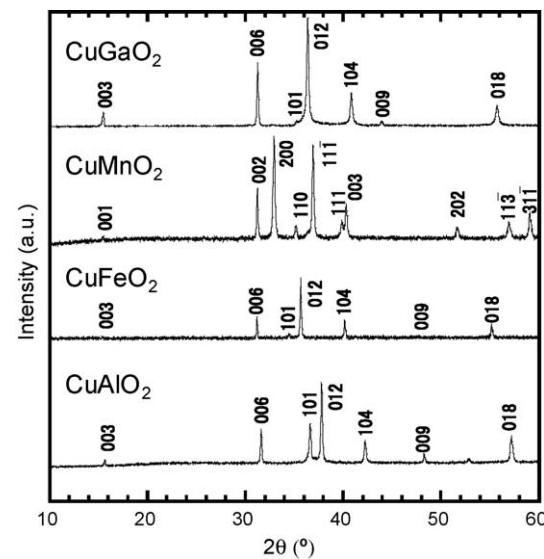


Fig. 2. XRD patterns for CuMO₂ (M = Al, Fe, Ga, Mn).

Table 1
Synthesis conditions and specific surface area (S) of CuMO₂ (M = Al, Fe, Mn, Ga).

M	Temperature (°C)	Heating time, h	Structure of product	S (m ² /g)
Fe	1100	6	3R-delafossite	1
Al	1150	24	3R-delafossite	1
Mn	960	36	Monoclinic	2
Ga	860	24	3R-delafossite	1

All the samples were heated in N₂ flow at 200 cm³/min.

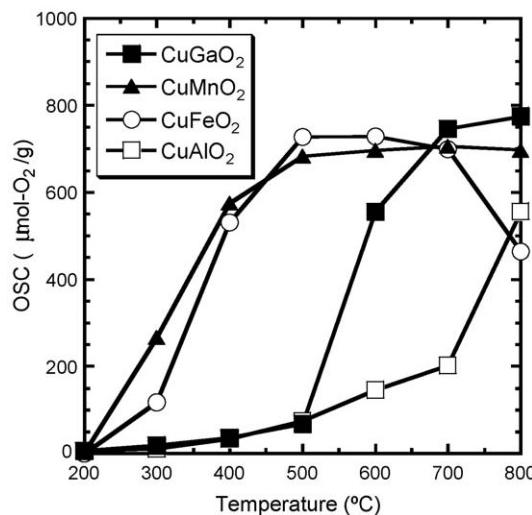


Fig. 3. OSC of CuMO₂ as a function of temperature.

CuGaO₂, the OSC reached 775 μmol-O₂/g at 800 °C, which is compared to the maximum value for CuFeO₂ and CuMnO₂. Fig. 4 shows XRD patterns of CuMO₂ samples after OSC measurement up to 800 °C. Partial decomposition of the delafossite phase was observed for CuFeO₂, CuMnO₂ and CuGaO₂. The peaks of metallic Cu were observed for those oxides, indicating reductive decomposition occurred. Moreover, Fe₃O₄ and Mn₃O₄ formed after decomposition of CuFeO₂ and CuMnO₂, respectively. The presence of Fe and Mn oxides including their divalent ions indicates that Fe³⁺ and Mn³⁺ in the delafossite-type oxides also reduced during the measurement. In the case of CuAlO₂, the delafossite phase remained as a single phase after the measurement. These results suggest that the stability of CuMO₂ delafossite-type oxide is affected by M³⁺ ions, which occupy the octahedral sites. As Fe³⁺ and Mn³⁺ are more easily reduced to divalent ions than Al³⁺ and Ga³⁺, decomposition of CuFeO₂ and CuMnO₂ would be caused by structural change of edge-shared MO₆ octahedra layer in reductive atmosphere.

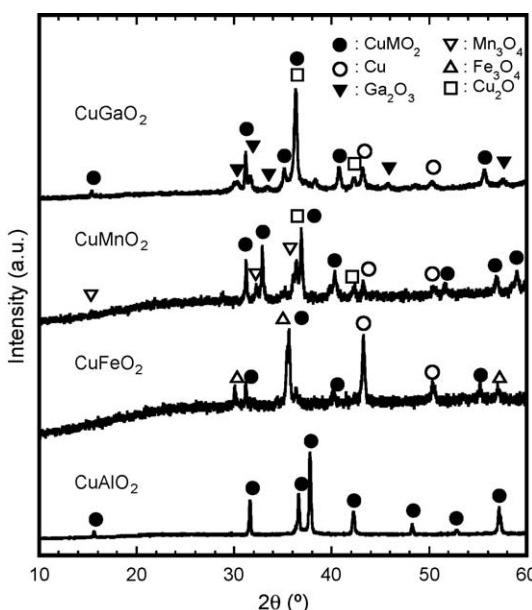


Fig. 4. XRD patterns of CuMO₂ samples after OSC measurement.

3.2. Oxidation and reduction behavior of CuMO₂

In order to investigate oxidation and reduction behavior of the delafossite phase during measurement of OSC, oxidized and reduced CuFeO₂ and CuMnO₂ samples were prepared by injection of O₂ or H₂ pulse at 300–600 °C. 25 or 50 mg of samples were used in order to change a W/F at the treatments, which were 0.0075 and 0.015 g s/cm³, respectively. Prior to these treatments, the samples were heated in He flow at 800 °C for 15 min. Fig. 5 shows XRD patterns of oxidized and reduced CuFeO₂. The delafossite-type CuFeO₂ remained as a single phase for the oxidized samples at 400–600 °C, while formation of Cu was observed for the reduced samples. Fig. 6 shows XRD patterns of reduced CuFeO₂ samples with a different W/F at 300 °C. The formation of Cu was also observed even at short contact time (W/F = 0.015). From a result of TPR measurement, reduction peak of these oxides observed below 350 and at 350–500 °C, for Cu₂O and Fe₂O₃, respectively, however, reduction of Cu oxide occurred without reduction of Fe³⁺ during the treatment. XRD patterns of oxidized and reduced CuMnO₂ are

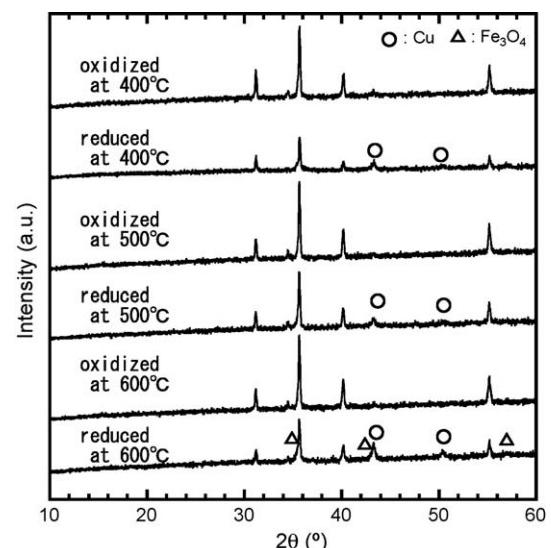


Fig. 5. XRD patterns of CuFeO₂ after oxidizing and reducing treatments (W/F = 0.0075 g s/cm³).

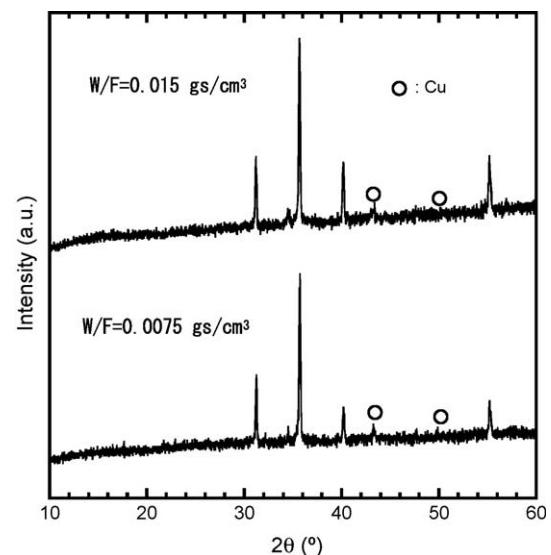


Fig. 6. XRD patterns of CuFeO₂ after reducing treatment at 350 °C.

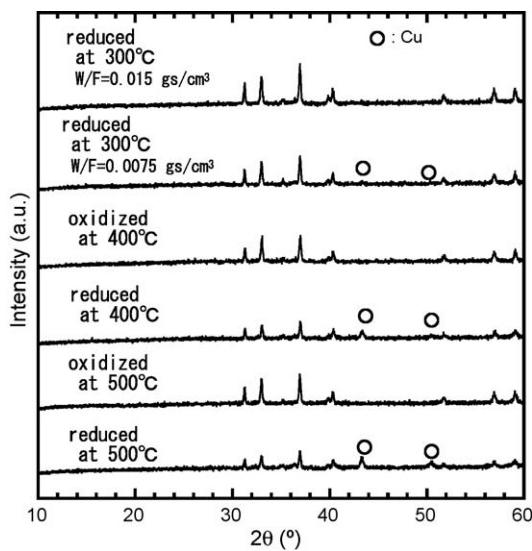


Fig. 7. XRD patterns of CuMnO₂ after oxidizing and reducing treatments.

shown in Fig. 7. In the case of oxidized samples, delafossite-type phases remained without Cu formation. For the reduced samples at 300–500 °C, Cu formation was observed and in the case of larger W/F at 300 °C, no metallic Cu formed even in reductive condition. Table 2 shows OSC values of CuFeO₂ and CuMnO₂ in different W/F conditions at 350 and 300 °C, respectively. The OSC values for CuFeO₂ were close to each other and smaller OSC was observed in the case of short contact time (W/F = 0.015) for CuMnO₂. These results suggest that non-stoichiometric delafossite phase of CuMnO₂ would be formed during oxidation/reduction process at low temperature for shorter contact time to H₂/He gas.

Table 2
OSC and W/F for CuFeO₂ and CuMnO₂.

Compound	Temperature (°C)	W/F (g s/cm ³)	OSC (μmol-O ₂ /g)
CuFeO ₂	350	0.015	211
CuFeO ₂	350	0.0075	205
CuMnO ₂	300	0.015	68
CuMnO ₂	300	0.0075	265

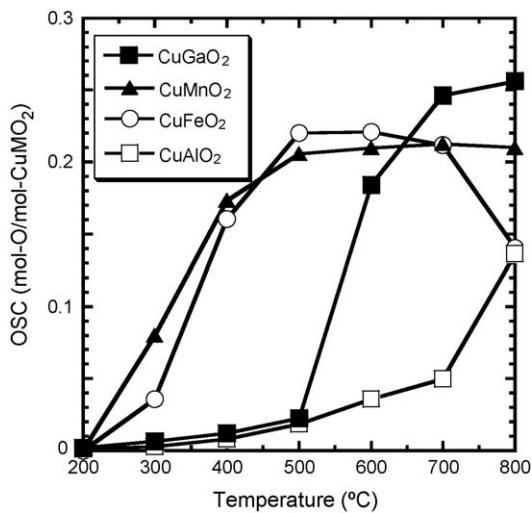


Fig. 8. Amount of oxygen atoms stored in 1 mol of CuMO₂ as a function of temperature.

Fig. 8 shows the OSC represented by amount of oxygen atoms stored in 1 mol of CuMO₂. The oxygen uptake of CuFeO₂ was 0.16 at 400 °C and increased up to 0.22 at 500 and 600 °C. Formation of non-stoichiometric CuFeO_{2+x} was reported by Zhao and co-workers [12] up to $x = 0.08$ and by Mugnier et al. [7] with x varying from 0 to 0.18. The oxygen uptake at 400–600 °C exceeded these amounts of extra oxygen, x and it was found from the XRD results of Fig. 5 that a reductive decomposition occurred at 400–600 °C. These results suggest that the excess oxygen uptake was due to oxidation/reduction cycle between Cu⁺ and Cu accompanying partial decomposition of CuFeO_{2+x}. For other delafossite oxides, CuMnO₂ and CuGaO₂, which decomposed during the OSC measurement, the OSC includes an oxygen uptake attributed to formation of metallic Cu by decomposition of the delafossite phase. In the case of CuAlO₂, which remained without decomposition below 800 °C, the oxygen uptake increased with temperature up to 0.13. The OSC value of CuAlO₂ is smaller than those of CuFeO₂, CuMnO₂ and CuGaO₂, while stability of CuAlO₂ against oxidation/reduction cycle below 800 °C is higher than that of CuFeO₂, CuMnO₂ and CuGaO₂.

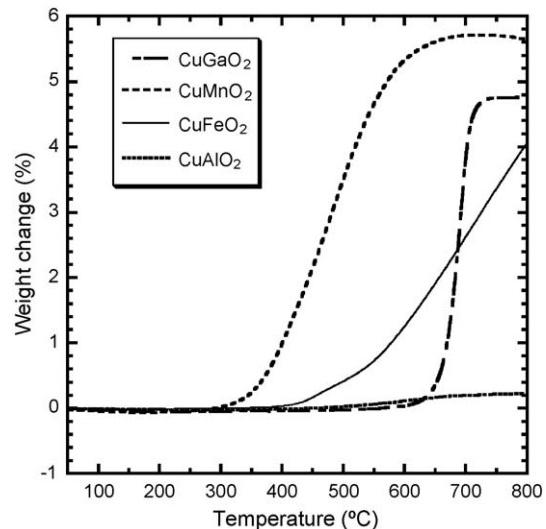


Fig. 9. TG curves of CuMO₂ measured in air.

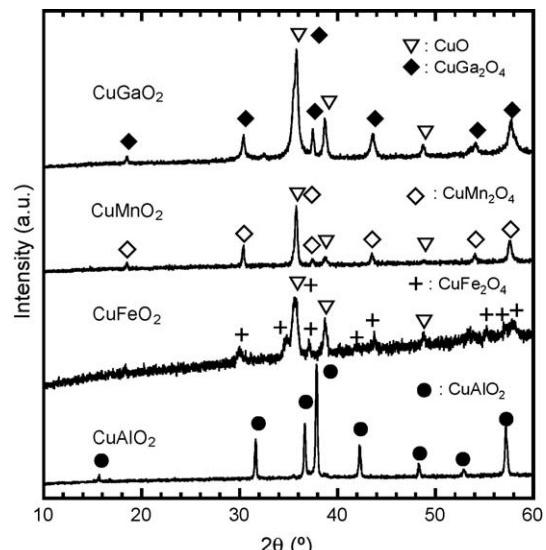
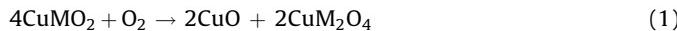


Fig. 10. XRD patterns of CuMO₂ after TG measurement.

Fig. 9 shows TG curves of CuMO₂ measured in air. Weight gains were observed for CuFeO₂, CuMnO₂ and CuGaO₂, while little weight change was observed for CuAlO₂. The XRD patterns of CuMO₂ after TG measurements are shown in Fig. 10. In the case of CuFeO₂, CuMnO₂ and CuGaO₂, diffraction peaks are observed for CuO and spinel phases such as CuFe₂O₄, CuMn₂O₄ and CuGa₂O₄, respectively. These products contain Cu²⁺ instead of Cu⁺ included in delafossite-type oxides. These results indicate that the weight gain observed in the TG curves accompanied oxidation of the delafossite-type oxides according to reaction (1):



Mugnier et al. [7] discussed a tendency for transformation of ABO₂ delafossite into spinel phase or non-stoichiometric ABO_{2+d} (B: trivalent ion) and reported that CuB₂O₄ spinel phases are stable for B³⁺ ions whose ionic radii are smaller than 0.0665 nm, such as Fe³⁺, Cr³⁺, Al³⁺ and Ga³⁺. However, in this study, no oxidative decomposition of CuAlO₂ occurred below 800 °C in air. Further investigation is necessary to confirm the effect of M³⁺ using other delafossite-type oxides, such as CuM_{1-x}M'_xO₂ solid solutions.

Reduction behavior of CuMO₂ was investigated by TPR measurement. TPR curves of CuMO₂, CuO and Cu₂O are shown in Fig. 11 and the XRD patterns of CuMO₂ after the measurements are shown in Fig. 12. Two TPR peaks were observed in the temperature ranges of 300–400 °C and 400–650 °C for CuFeO₂. For CuMnO₂, two peaks were also observed in the 250–400 °C range. CuO and Cu₂O were reduced to Cu at 250 and 540 °C, respectively. As reduction of Fe or Mn oxides occurs at higher temperature than reduction of Cu oxide in reductive atmosphere, the reduction peaks observed at lower temperature for CuFeO₂ and CuMnO₂ would be attributed to reduction of Cu⁺, leading to decomposition of the delafossite phases.

The diffraction peaks of Fe and FeO were observed in the XRD pattern for CuFeO₂, indicating Fe³⁺ in CuFeO₂ was reduced to Fe²⁺ or Fe during the TPR measurement. Therefore, the peak observed at higher temperature would be attributed to reduction of Fe³⁺ in CuFeO₂. In reductive condition of the OSC measurement using pulse injection, Fe₃O₄ formed instead of Fe and FeO, because reaction time between CuFeO₂ and H₂ for pulse injection was much shorter than that for the TPR measurement. In the case of CuMnO₂, as formation of MnO was observed by the XRD measurement, the

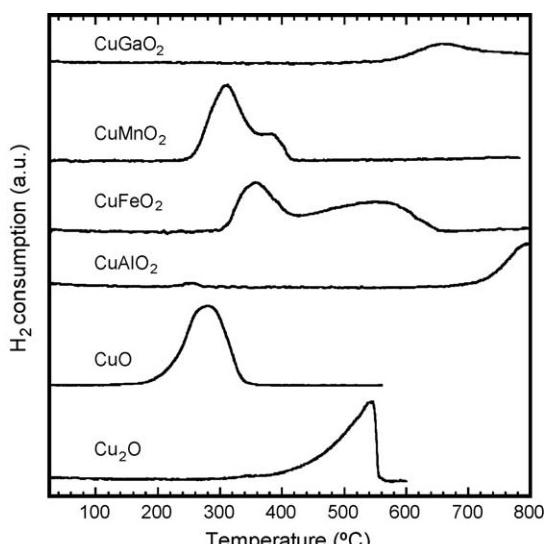


Fig. 11. TPR curves of CuMO₂ and Cu oxides.

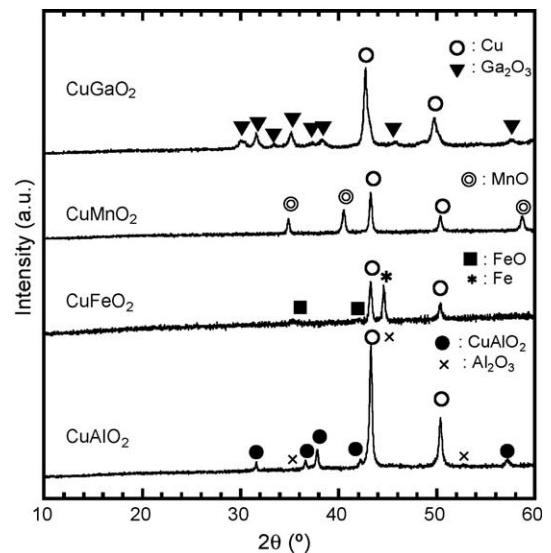


Fig. 12. XRD patterns of CuMO₂ after TPR measurement.

TPR peak at 350–400 °C would be due to reduction of Mn³⁺ to Mn²⁺. For CuAlO₂ and CuGaO₂, reduction occurred above 700 °C and at 550–700 °C, respectively. Particularly, a small amount of the delafossite phase remained for CuAlO₂. These results indicate that durability of CuAlO₂ against reductive atmosphere is higher than that of CuFeO₂ and CuMnO₂, suggesting that reducibility of Cu⁺ in CuMO₂ can be controlled by M ions at the octahedral sites.

The conventional TWC contains CeO₂-based oxide as oxygen storage component. CeO₂ exhibits oxygen storage/release behavior accompanying the following reactions including the change in oxidation state of Ce.



According to reaction (3), the maximum amount of O₂ which is released from 1 mol of CeO₂ is 0.25 mol. However, total OSC value (mol-O₂/mol-Ce) estimated by TG measurement in 20% H₂-N₂ gas is less than 0.1 at 300 °C [13]. And the reversible OSC (mol-O₂/mol-CeO₂) of Pt/CeO₂/Al₂O₃ catalyst estimated by H₂/O₂ pulse injection reported by Kakuta et al. [14] is less than 0.05 at 773–1173 K. The OSC of the delafossite-type CuMnO₂ was 0.04 mol-O₂/mol-CuMO₂ (0.08 mol-O/mol-CuMO₂) at 300 °C, which is comparable to that of the Pt/CeO₂/Al₂O₃ catalyst. This suggests that the degrees of reversible oxygen storage/release ability for 1 mol of CuMnO₂ are comparable to that of CeO₂ at low temperature, however, these delafossite oxides decomposed under oxidation/reduction cycle above 400 °C.

4. Conclusions

Delafossite-type CuMO₂ (M = Fe, Mn, Al, Ga) exhibited oxygen storage capacity under oxidation/reduction cycle. OSC values of CuFeO₂ and CuMnO₂ at low temperature (<500 °C) are larger than those for CuAlO₂, CuGaO₂ and CeO₂-based materials. The large OSC includes an oxygen uptake at low temperature attributed to formation of metallic Cu by decomposition of the delafossite phase for CuFeO₂ and CuMnO₂. In the case of CuAlO₂, which remained without decomposition below 800 °C, the oxygen uptake increased with temperature up to 0.13 mol-O/mol-CuMO₂. In order to use the copper containing delafossite-type oxides as an OSC material for a commercial TWC, the further research is necessary to improve the stability at high temperature in oxidative or reductive

atmosphere. In this study, it was found that the oxygen storage behavior of delafossite-type CuMO₂ compounds can be controlled by a combination of Cu and M ions, therefore, CuM_{1-x}M'_xO₂ solid solutions may be candidate materials which are stable in oxidative and reductive atmospheres at high temperature.

References

- [1] H.C. Yao, Y.F. Yu Yao, *J. Catal.* 86 (1984) 254–265.
- [2] J. Kašpar, P. Fornasiero, M. Graziani, *Catal. Today* 50 (1999) 285–298.
- [3] A. Morikawa, T. Suzuki, T. Kanazawa, K. Kimura, A. Suda, H. Shinjo, *Appl. Catal. B* 78 (2008) 210–221.
- [4] S. Royer, H. Alamdari, D. Duprez, S. Kaliaguine, *Appl. Catal. B* 58 (2005) 273–288.
- [5] M. Sugiura, M. Ozawa, A. Suda, T. Suzuki, T. Kanazawa, *Bull. Chem. Soc. Jpn.* 78 (2005) 752–767.
- [6] R.J. Cava, H.W. Zandbergen, A.P. Ramirez, H. Takagi, C.T. Chen, J.J. Krajewski, W.F. Peck Jr., J.V. Waszczak, G. Meigs, R.S. Roth, L.F. Schneemeyer, *J. Solid State Chem.* 104 (1993) 437–452.
- [7] E. Mugnier, A. Barnabe, P. Tailhades, *Solid State Ionics* 177 (2006) 607–612.
- [8] K. Isawa, Y. Yaegashi, M. Komatsu, M. Nagano, S. Sudo, *Phys. Rev. B* 56 (1997) 3457–3466.
- [9] M. Trari, J. Topfer, J.P. Doumerc, M. Pouchard, A. Ammar, P. Hagenmuller, *J. Solid State Chem.* 111 (1994) 104–110.
- [10] K. Hayashi, H. Hayashida, Y. Nakano, J. Meta, *Nanocryst. Mater.* 20–21 (2004) 563–570.
- [11] J. Topfer, M. Trari, P. Gravereau, J.P. Chaminade, J.P. Doumerc, *Z. Krist.* 210 (1995) 184–187.
- [12] M. Hassegawa, M.I. Batrashevich, T.R. Zhao, H. Takei, T. Goto, *Phys. Rev. B* 63 (2001) 184437.
- [13] A. Suda, H. Sobukawa, T. Suzuki, T. Kandori, Y. Ukyo, M. Sugiura, *J. Ceram. Soc. Jpn.* 109 (2001) 177–180.
- [14] N. Kakuta, N. Morishima, M. Kotobuki, T. Iwase, T. Mizushima, Y. Sato, S. Matsuura, *Appl. Surf. Sci.* 121/122 (1997) 408–412.